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EFFECTS OF TEMPERATURE GRADIENTS, SELF-ABSORPTION, AND SPECTRAL LINE-SHAPE ON APPARENT ROTATIONAL TEMPERATURES OF OH

by

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March 1953

EFFECTS OF TEMPERATURE GRADIENTS, SELF-ABSORPTION, AND SPECTRAL LINE-SHAPE ON APPARENT ROTATIONAL TEMPERATURES OF OH*

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B. H. Elliott †

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The effects of temperature gradients, line contour, and self-absorption on observable intensities have been studied for the P_1 -branch, (0,0)-band, $\stackrel{\circ}{\Sigma} \rightarrow \stackrel{\circ}{\longrightarrow} \mathbb{I}$ transitions of OH in absorption and emission experiments.

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tt. Colonel, U.S.M.C. This article is based, in part, on a thesis submitted by B. H. Elliott to the Graduate School of the California Institute of Technology, in partial fulfillment of requirements for the degree of Aeronautical Engineer. The author is indebted to Dr. S. S. Penner for helpful suggestions throughout the course of the work.

The effects on apparent rotational temperatures (of OH) of temperature gradients and of spectral line-shape, coupled with 2,3 varying degrees of self-absorption, have been described for representative systems. It is the purpose of the present calculations to amplify the conclusions drawn previously in several respects by presenting additional numerical results particularly for simplified models of low-pressure and atmospheric - pressure flames.

The calculations emphasize the fact that definitive conclusions regarding interpretation of flame spectra are not easy to obtain by use of conventional low-resolution spectroscopic studies of flames. Multiple path experiments or absorption studies with discrete line sources appear promising provided they are restricted to conditions under which the spectral line-shape is known. Alternately, the use of interferometric studies may be indicated.

I. Effect of Line -Shape and of Self-Absorption on the Use of the Isointensity Method³ for Isothermal Systems.

According to the isointensity method the temperature of a radiator is obtained from a comparison of two spectral lines which are of equal intensity. Let A(K) be the total intensity of the line identified by the

S. S. Penner, "Effect of Spectral Line-Shape on Apparent Rotational Temperatures of OH", Technical Report No. 8, November 1952; Journal of Chemical Physics (in press).

G. H. Dieke and H. M. Crosswhite, "The Ultraviolet Bands of OH, Fundamental Data," Bumblebee Series Report No. 87, Nov. 1948.

S. S. Penner, "Quantitative Studies of Apparent Rotational Temperatures of OH in Emission and Absorption (Spectral Lines With Doppler Contour)", Technical Report No. 5, September 1952; Journal of Chemical Physics (in press).

index K. Then, for spectral lines with Doppler contour, 1

$$A(K)/A(K') = \left[1_{\max}(K)/I_{\max}(K')\right] \left[\mathcal{V}_{L_{\mathbf{u}}}(K)/\mathcal{V}_{L_{\mathbf{u}}}(K')\right] \times \left[\xi(K')/\xi(K)\right]$$
(1)

where $I_{max}(K)$ is the peak intensity emitted from the K'th line, $\mathcal{D}_{L_1}(K)$ is the frequency at the line center of the K'th line, and $\xi(K)$ is a known function of the value of $P_{max}(K)$ for the K'th line, where $P_{max}(K)$ is the maximum spectral absorption coefficient and K is the optical density. The line-shape for combined Doppler-and collision-broadening is described by the parameter

$$a = (b_N + b_C) (\ln 2)^{1/2}/b_D$$
 (2)

where b_N , b_C , and b_D denote, respectively, the natural, the collision, and Doppler half-widths. In general $b_N << b_C$ and $a \simeq 0$ for pure Doppler - broadening.

In order to emphasize that Eq. (1) applies to spectral lines with Doppler contour we shall write it as

0

120

$$A(a = 0, K)/A(a = 0, K') = \left[I_{\max}(a = 0, K)/I_{\max}(a = 0, K')\right]$$

$$\times \left[\mathcal{V}_{\ell_{\mathbf{u}}}(K)/\mathcal{V}_{\ell_{\mathbf{u}}}(K')\right] \left[\xi(K')/\xi(K)\right]. \tag{1a}$$

The effect of line-shape, under isothermal conditions, on the use of the isointensity method may be determined by evaluating the ratio A(a, K)/A(a, K'). This result can be obtained most conveniently by using Eq. (la) in conjunction with the "curves of growth". 4

E. M. F. van der Held, Z. Physik 70, 508 (1931); A Unsold, Physik der Sternatmosphären, p. 168, J. W. Edwards, Ann Arbor 1948; for an extension of the curves of growth to larger values of the line-shape parameter a, see S. S. Penner and R. W. Kavanagh, Technical Report No. 6, Contract Nonr-220 (03), NR 015 210, California Institute of Technology, September 1952, or Journal of the Optical Society of America (in press).

The ordinate of the curve of growth is proportional to A(a, K) for $P_{\max} X(K)$. Thus the ratio A(a, K)/A(a = 0, K) can be obtained simply by reading the ordinate corresponding to the known value of $P_{\max} X(K)$. Finally, the quantity A(a, K)/A(a, K') is obtained by writing

$$A(a, K)/A(a, K') = \left\{ \left[A(a, K)/A(a = 0, K) \right] / \left[A(a, K')/A(a = 0, K') \right] \right\}$$

$$\times \left[A(a = 0, K)/A(a = 0, K') \right]. \tag{3}$$

The results for K' = 1 of representative calculations at 3000° K, using Eqs. (1a) and (3) together with the "curves of growth" [for the P_1 -branch of the $^2\Sigma \rightarrow 2\Pi$ transitions of OH, (0,0)-band], are plotted in Figs. 1 to 3 for a = 0.005, a = 0.05, and a = 2, respectively.* The self-absorption parameter \mathcal{E}' again refers to the value of 1 - exp (- P_{max} X) for the first line of the P_1 -branch and assumes the values 0.3, 0.7, and 0.95.

0

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In order to illustrate the combined effects of line-shape and self-absorption on lines of equal intensity, from which conclusions might be drawn concerning the "temperature", the results listed in Table I may be consulted. In Table I the lines of intensity closest to the intensity for K = 3 and K = 6 have been tabulated for different values of & and of a. Reference to the data shown in Table I indicates a large effect of & for small a, but the results are quite insensitive to & for large a. Hence the conclusion is reached that self-absorption errors become more important as the pressure is reduced, i.e., as a is decreased. A more quantitative conclusion

^{*} The authors are indebted to Mr. N. Schroeder for performing the numerical calculations.

is justified only if absolute values are known for a in flames, which is not the case at the present time.

Table I.	Effect of & and	a on Lines of Equal Tot	al Intensity.		
K value of line with intensity closest to K = 3 for					
COTY TO THE	€' = 0.3	€¹ ± 0.7	£' = 0.95		
a = 0.005	volation da 13 liv X	14	16		
a = 0.05	13	14	16		
a = 2	13	13	14		
**************************************	K value of line v	with intensity closest to	K = 6 for		
ition () a	£' = 0.3	€¹ = 0.7	٤ ' = 0.95		
a = 0.005	10	11	14		
a = 0.05	10	11	13		
a = 2	10	10	10		

Because of the ambiguity in matching lines of equal intensity for small values of a and large values of \mathcal{E}^{\dagger} the isointensity method cannot be used, even for isothermal systems, at low pressures unless independent proof is provided that $\mathcal{E}^{\dagger} << 0.3$.

If E' is sufficiently small then it can be shown that

$$A(a,K)/A(a,K') = S_{Iu}(K)/S_{Iu}(K')$$
 (4)

where $S_{Lu}(K)$ is the integral of the spectral absorption coefficient for the K'th line. Here $S_{Lu}(K)$ is given by the expression 5

⁵ S. S. Penner, J. Chem. Phys. 20, 507 (1952).

$$\mathbf{S}_{\mathbf{L}\mathbf{u}}(\mathbf{K}) = (64\pi^{4}/3/c^{3}) \, \mathbf{N}_{\mathbf{u}}(\mathbf{K}) \left[\mathbf{V}_{\mathbf{u}}(\mathbf{K}) \right]^{4} \left[\mathbf{G}_{\mathbf{L}\mathbf{u}}(\mathbf{K}) \right]^{2} / c \, \mathcal{O} \left[\mathbf{V}_{\mathbf{u}}(\mathbf{K}) \right]$$
 (5)

where c = velocity of light; N_u = number of molecules per unit volume per unit pressure in the upper energy state; \mathcal{V}_{Lu} = frequency of the emitted or absorbed radiation at the center of the line, which is obtained from the Bohr frequency relation; q_{Lu} = matrix element corresponding to transitions between the two given energy states; and $\int_{Lu}^{\infty} (\mathcal{V}_{Lu}) = \text{volume density of blackbody radiation at the frequency } \mathcal{V}_{Lu}$ as given by the Planck distribution law. The quantity $N_u(K)$ may be replaced by $N_u(K) = Ng_u(K) \left[\exp(-E_u(K)/kTu) \right] / \Omega$ where N = total number of molecules per unit volume per unit pressure, $g_u(K) = \text{statistical weight of the upper energy state involved in the given transition, <math>\Omega = \text{complete partition function, and the expression for } S_{Lu}(K)$ may be rewritten as

$$S_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}) = (64\pi^{4}/3c^{3}) N_{\mathcal{B}_{\mathbf{u}}}(\mathbf{K}) \left[\mathcal{V}_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}) \right]^{4} \left[q_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}) \right]^{2}$$

$$\times \left\{ \exp \left[-E_{\mathbf{u}}(\mathbf{K})/kT\mathbf{u} \right] \right\} Q^{-1} e^{-1} \left\{ \int_{\mathbf{u}}^{0} \left[\mathcal{V}_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}) \right] \right\}^{-1}. \quad (5a)$$

Hence, for lines of equal intensity,

$$S_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K})/S_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}') = \left\{ \left[\mathcal{I}_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}) \right]^{4} g_{\mathbf{u}}(\mathbf{K}) \left[q_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}) \right]^{2} \right\}$$

$$\times \left\{ \left[\mathcal{I}_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}') \right]^{4} g_{\mathbf{u}}(\mathbf{K}') \left[q_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}') \right]^{2} \right\}^{-1}$$

$$\times \left\{ \mathcal{S}^{\circ} \left[\mathcal{I}_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}') \right] \right\} \left\{ \mathcal{S}^{\circ} \left[\mathcal{I}_{\mathcal{L}_{\mathbf{u}}}(\mathbf{K}) \right] \right\}^{-1}$$

$$\times \exp \left\{ - \left[E_{\mathbf{u}}(\mathbf{K}) - E_{\mathbf{u}}(\mathbf{K}') \right] / kT_{\mathbf{u}} \right\} \equiv 1$$
(6)

But

Substituting this relation in Eq. (6) we obtain

$$1 = \left[\mathcal{V}_{Q_{\mathbf{u}}}(\mathbf{K}) / \mathcal{V}_{Q_{\mathbf{u}}}(\mathbf{K}') \right] \left\{ \mathbf{g}_{\mathbf{u}}(\mathbf{K}) \left[\mathbf{q}_{Q_{\mathbf{u}}}(\mathbf{K}) \right]^{2} / \mathbf{g}_{\mathbf{u}}(\mathbf{K}') \left[\mathbf{q}_{Q_{\mathbf{u}}}(\mathbf{K}') \right]^{2} \right\}$$

$$\times \exp \left\{ - \left[\mathbf{E}_{\mathbf{u}}(\mathbf{K}) - \mathbf{E}_{\mathbf{u}}(\mathbf{K}') \right] / \mathbf{k} \mathbf{T}_{\mathbf{u}} \right\}$$

$$\times \exp \left\{ (\mathbf{h}/\mathbf{k} \cdot \mathbf{T}_{\mathbf{u}}) \left[\mathcal{V}_{Q_{\mathbf{u}}}(\mathbf{K}) - \mathcal{V}_{Q_{\mathbf{u}}}(\mathbf{K}') \right] \right\}$$
(6a)

In this last expression every quantity is known for a given pair of lines, except the temperature T_u . Hence Eq. (6a) can be used to obtain T_u as

$$T_{u} = -\frac{\left[E_{u}(K) - E_{u}(K')\right] + h\left[\mathcal{V}_{\mathcal{L}_{u}}(K) - \mathcal{V}_{\mathcal{L}_{u}}(K')\right]}{k \ln \left\{\frac{\mathcal{V}_{\mathcal{L}_{u}}(K') - g_{u}(K')}{\mathcal{V}_{\mathcal{L}_{u}}(K) - g_{u}(K')}\right]^{2}}\right\}$$
(6b)

This principle is used in conventional isointensity methods for measuring temperatures although the approximation $\mathcal{V}_{\mathcal{L}_{\mathbf{u}}}(K) \simeq \mathcal{V}_{\mathcal{L}_{\mathbf{u}}}(K)$ is usually added,

It is clear from the preceeding discussion that the practical use of Eq. (6b) depends on the identity of A(a, K)/A(a, K') with $S_{L_{\mathbf{u}}}(K)/S_{L_{\mathbf{u}}}(K')$. The limitations concerning this relation have been discussed in connection with Figs. 1 to 3 and Table 1.

II. Two-Path Experiments for Non-Isothermal Regions (Spectral Lines with Doppler Contour, Peak Intensities).

Calculations which are made in this section correspond to the assumed experimental arrangement illustrated in Fig. 4.

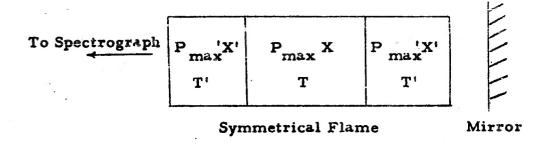


Fig. 4. Schematic arrangement of two-path experiment for a flame represented by two isothermal regions.

The OH concentration is treated as a variable parameter both in the hot region $\left\{\mathcal{E} = \begin{bmatrix} 1 - \exp(-P_{\max} X) \end{bmatrix}\right\}$ and in the cool region $\left\{\mathcal{E}' = \begin{bmatrix} 1 - \exp(-P_{\max}'X') \end{bmatrix}\right\}$. It is physically reasonable to assume $\mathcal{E}' \leq \mathcal{E}$.

Calculations have been carried out for <u>peak</u> intensities and for spectral lines with Doppler Contour. Peak intensities, even for low-pressure flames with Doppler-broadened lines, have not been measured. Such measurements might be possible with an interferometer. In particular, it is clear that the results of the present calculations do not apply to observational data obtained with a low-resolution spectrograph.

Referring to Fig. 4 the peak intensity I for the spectral line whose center lies at \mathcal{V}_{Lu} may be written as follows:

$$I = R'(\mathcal{V}_{u}) \left[1 - \exp(-P_{\max}'X') \right] + R(\mathcal{V}_{u}) \left[1 - \exp(-P_{\max}X) \right] \exp(-P_{\max}'X')$$

$$+ R'(\mathcal{V}_{u}) \left[1 - \exp(-P_{\max}'X') \right] \exp(-P_{\max}X) \exp(-P_{\max}'X')$$

$$+ r \left\{ R'(\mathcal{V}_{u}) \left[1 - \exp(-P_{\max}'X') \right] \exp(-2P_{\max}'X') \exp(-P_{\max}X) \right\}$$

$$+ R(\mathcal{V}_{u}) \left[1 - \exp(-P_{\max}X) \right] \exp(-3P_{\max}'X') \exp(-P_{\max}X)$$

$$+ R'(\mathcal{V}_{u}) \left[1 - \exp(-P_{\max}X) \right] \exp(-2P_{\max}X) \exp(-3P_{\max}X')$$

$$+ R'(\mathcal{V}_{u}) \left[1 - \exp(-P_{\max}X) \right] \exp(-2P_{\max}X) \exp(-3P_{\max}X')$$

where r is the reflectivity of the mirror and the other symbols have their usual meaning. Equation (7) may be rewritten in the form

$$I = R' (\mathcal{V}_{u}) \left[1 - \exp(-P_{\max}'X') \right]$$

$$\left\{ 1 + \exp(-P_{\max} X - P_{\max}'X') + r \cdot \exp(-P_{\max} X - 2 P_{\max}'X') \right\}$$

$$+ r \cdot \exp(-2 P_{\max} X - 3 P_{\max}' X') \right\}$$

$$+ R (\mathcal{V}_{u}) \left[1 - \exp(-P_{\max} X) \right] \cdot \exp(-P_{\max}' X')$$

$$\left\{ 1 + r \cdot \exp(-P_{\max} X - 2 P_{\max}'X') \right\}.$$
(7a)

Using Planck's blackbody distribution for R(ν_{g_u}) it follows that

$$R'(\mathcal{V}_{\mathcal{U}})/R(\mathcal{V}_{\mathcal{U}}) = \exp\left\{-\left(h\mathcal{V}_{\mathcal{U}}/k\right)\left[\left(1/T'\right) - \left(1/T\right)\right]\right\}.$$

Hence Eq. (7a) becomes

0

(1)

$$I/R (V_{u}) = \left[1 - \exp(-P_{\max} X) \right] \exp(-P_{\max}'X')$$

$$\left\{ 1 + r \exp(-P_{\max} X - 2 P_{\max}'X') \right\}$$

$$+ \exp\left\{ -(hV_{u}/k) \left[(1/T') - (1/T) \right] \left[1 - \exp(-P_{\max}'X') \right] \right\}$$

$$\times \left\{ 1 + \exp(-P_{\max} X - P_{\max}'X') + r \exp(-P_{\max} X - 2 P_{\max}'X') + r \exp(-P_{\max} X - 2 P_{\max}'X') \right\}. \tag{7b}$$

For reasonable values of T and T' and for unit reflectivity of the mirror we obtain:

$$I \simeq R(V_{\mathcal{L}_{\mathbf{u}}}) \mathcal{E} (1 - \mathcal{E}') \left[1 + (1 - \mathcal{E}) (1 - \mathcal{E}')^{2} \right]$$
 (8)

If I' represents the intensity for the single path, then $I' \cong R(\mathcal{V}_{\mathcal{L}_{\mathbf{u}}}) \mathcal{E}$ (1 -&') whence

(0)

D

$$I/I' \simeq 1 + (1 - \mathcal{E}) (1 - \mathcal{E}')^2.$$
 (9)

The observable ratio I/I' has been calculated as a function of $\frac{K}{K}$ for various values of $\mathcal{E}(K=1)$ and $\mathcal{E}'(K=1)$ for the P_1 - branch and P_1 transitions of OH. Results are plotted in Figs. 5 to 3. Reference to Figs. 5 to 8 shows that the intensity ratio P_1 is a very sensitive function of the self absorption parameters \mathcal{E} and \mathcal{E}' . It is clear that the intensity ratio for two-path experiments would be a much less sensitive function of \mathcal{E} and \mathcal{E}' for measurements of total intensity.

The important result derived from the present calculations is that even for values of \mathcal{L} as small as 0.3 the ratio I(K)/I(K') is appreciably less than two for the stronger lines. In other words, a

two-path experiment measuring peak intensities is a relatively sensitive device for studying self-absorption and temperature-distortion quantitatively. As will be shown in the following Section III, this last conclusion applies also to absorption experiments in which peak intensities are measured.

III. Absorption Experiment for Non-Isothermal Regions (Spectral Lines with Doppler Contour, Peak Intensities).

Because of the experimental difficulties arising from inadequate resolving power in the measurement of peak intensities for two-path experiments, it is of interest to consider the use of absorption experiments using discrete line sources.

Calculations which are made in this section correspond to the assumed experimental arrangement illustrated in Fig. 9. The light source radiates at the center of a given spectral line as a blackbody at the temperature T_a.

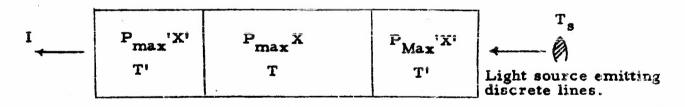


Fig. 9. Schematic arrangement of absorption experiment for a flame represented by two isothermal regions.

Referring to Fig. 9, the transmitted intensity I for the spectral line whose center lies at $\mathcal{V}_{\ell u}$ may be written as follows:

$$I = R(T_s) \exp(-2 P_{max}'X' - P_{max}'X) + R(T') \left[1 - \exp(-P_{max}'X')\right] + R(T) \left[1 - \exp(-P_{max}'X)\right] \exp(-P_{max}'X') + R(T') \left[1 - \exp(-P_{max}'X')\right] \exp(-P_{max}'X').$$
(10)

For
$$T_s >> T$$
, T^t and $\exp (-P_{max}X)$, $\exp (-P_{max}X) << 1$,

$$I = R(T_s) \exp (-2 P_{max}X). \tag{10a}$$

From Eq. (10):

$$I/R(T_s) = \exp(-2 P_{\max}'X' - P_{\max}X) + R(T')/R(T_s) \left[1 - \exp(-P_{\max}'X')\right] \left[1 + \exp(-P_{\max}X - P_{\max}'X')\right] + R(T)/R(T_s) \left[1 - \exp(-P_{\max}X)\right] \exp(-P_{\max}'X')$$
(10b)

OT

$$I/R(T_{s}) = \exp(-2 P_{\max}^{!} X^{!} - P_{\max}^{!} X)$$

$$+ \exp\left\{-(h \mathcal{V}_{\ell_{l}}/k) \left[(1/T^{!}) - (1/T_{s}) \right] \right\} \left[1 - \exp(-P_{\max}^{!} X^{!}) \right]$$

$$\times \left[1 - \exp(-P_{\max}^{!} X - P_{\max}^{!} X^{!}) \right]$$

$$+ \exp\left\{-(h \mathcal{V}_{\ell_{l}}/k) \left[(1/T^{!}) - (1/T_{s}) \right] \right\} \left[1 - \exp(-P_{\max}^{!} X) \right] \exp(-P_{\max}^{!} X^{!}).$$
(10c)

In general we may neglect the radiation from the region at temperature T' and use the relation

$$I/R(T_s) = \exp(-2 P_{\max}'X' - P_{\max}X) + \exp\{-(hV_{u}/k)[(1/T) - (1/T_s)]\}[1 - \exp(-P_{\max}X)] \exp(-P_{\max}X')] + \exp\{-(hV_{u}/k)[(1/T) - (1/T_s)]\}. (10d)$$

If $T_g >> T$, as should be the case for a good absorption experiment, then

$$\exp\left\{-(h\mathcal{V}_{lu}/k)\left[(1/T)-(1/T_s)\right]\right\}\simeq \exp\left(-h\mathcal{V}_{lu}/kT\right).$$

But $hV/k = hc\omega/k = 1.432\omega$ and $exp(-hV_{gu}/kT) \approx exp(-1.432x30,000/3000) \approx exp(-14)$.

Hence for T >>> T Eq. (10d) may be written as

$$I/R(T_s) \simeq (1 - \mathcal{E}')^2 (1 - \mathcal{E}). \tag{11}$$

Comparison of Eqs. (9) and (11) shows that the transmitted intensity divided by the incident intensity from a discrete line source is nearly equal to I/I' - 1 where I/I' is the ratio of the intensity of the flame for a double-path experiment to the intensity of the flame for a single-path experiment. Figures (5) to (8) may then be reinterpreted in such a way that I/I' - 1 represents the absorptivity of the flame for discrete radiation.

Since 1/1' or 1/1' - 1, for measurements of peak intensities, are very sensitive functions of the self absorption parameters \mathcal{E} and \mathcal{E}' , it follows that $1/R(T_g)$ is also a sensitive function of \mathcal{E} and \mathcal{E}' . Unlike peak intensity determinations in two-path experiments, the discrete line source experiment may be feasible with ordinary spectroscopic apparatus by using as source OH in a discharge tube or else an excited

metal line which coincides exactly with a line of OH.* In this connection it is of interest to note that the 3063.97Å line of tungsten coincides with the 10° line of the (0,0) band, $^2\sum \rightarrow ^2\prod$ transitions of OH.

IV. Two-Path Experiments for Non-Isothermal Regions (Spectral Lines with Combined Doppler and Collision Broadening; Real Taleasities).

The calculations summarized in this section again correspond to the experimental arrangement illustrated in Fig. 4 of Section II. The parameter P_{max} must now be replaced by $P(\omega_{Au})$ where $P(\omega_{Au})$, the spectral absorption coefficient at the line center, is to be evaluated for combined Doppler- and collision-broadening. The quantity $P(\omega_{Au})$ is related to P_{max} and a through the expression $\frac{4}{3}$

$$P(\omega_{\ell u}) = P_{max} \left[\exp(a^2) \right] \left[\operatorname{erfc}(a) \right]$$
 (12)

where

6

exfc (a) =
$$\left[\frac{2}{1!}\left(\frac{1}{2}\right)\right]$$
 $\left[\exp\left(-x^2\right)\right]$ dx.

Equation (9) may be rewritten as

$$1/I' \simeq 1 + (1 - \mathcal{E}_{D-C}) (1 - \mathcal{E}_{D-C})^2$$
 (9a)

where

$$\mathcal{E}_{D-C} = 1 - \exp \left[-(P_{mix} X) \operatorname{erfc}(a) \exp(a^2) \right], \qquad (13)$$

$$\mathcal{E}_{D-C}^{i} = 1 - \exp\left[-(P_{\max}^{i}X^{i}) \operatorname{erfc}(a^{i}) \exp(a^{i}^{2})\right],$$
 (13a)

and a' represents the line-shape parameter for the gases at the temperature T'.

^{*} Absorption experiments using discrete lines as source have been considered at various times by most of the active workers in combustion spectroscopy.

The ratio I/I' has been calculated for a' = a ranging from 0 to 10, ξ (K = 1) = 0.7, ξ '(K = 1) = 0.1 and 0.5, for the P₁-branch, (0,0)-band and $^2\sum \rightarrow ^2\prod$ transitions of OH. Results are plotted in Figs. 10 and 11. Reference to Figs. 10 and 11 shows that two-path experiments will yield results which are sensitive functions of the line-shape parameter a, with distortion of experimental data by self-absorption diminishing as the numerical value of a is increased, under otherwise comparable experimental conditions.

V. Peak Absorption Experiments for Non-Isothermal Regions (Spectral Lines with Combined Doppler and Collision Broadening)

Calculations in this section correspond to the experimental arrangement illustrated in Fig. 9 of Section III with P_{max} replaced by $P(\omega_{fu})$. Here $P(\omega_{fu})$ again depends on P_{max} and a as shown in Eq. (12).

Equation (11) now becomes

 (\cap)

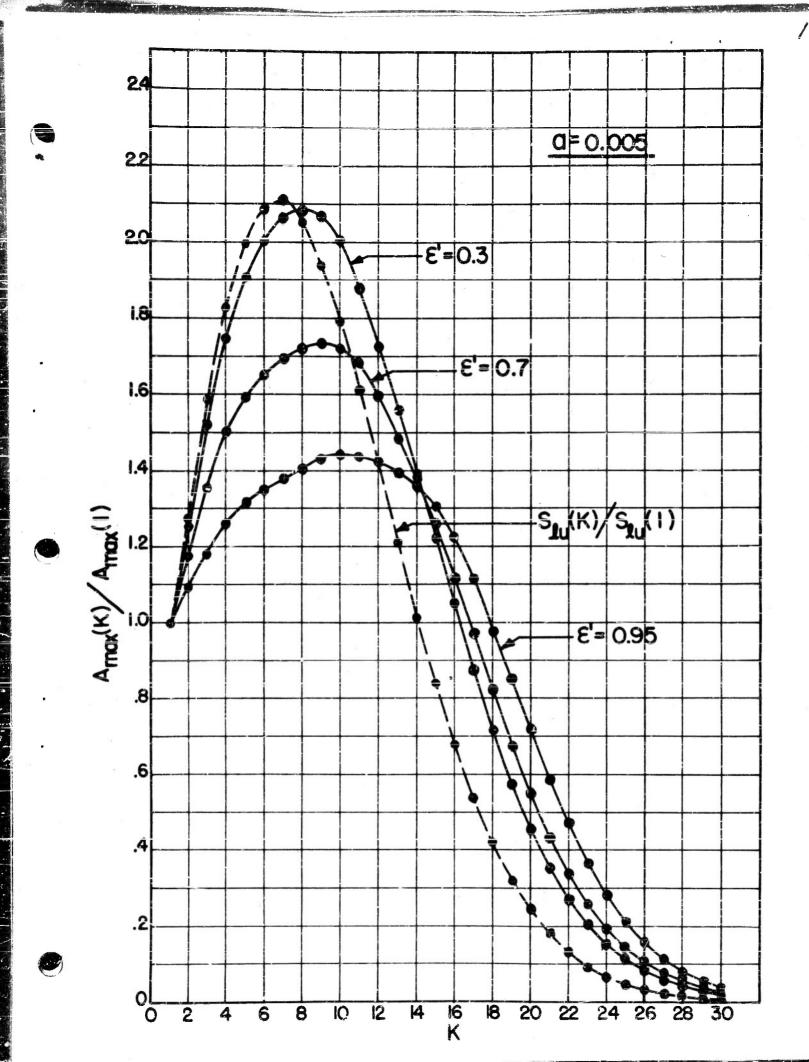
$$I/R(T_s) \simeq (1 - \epsilon_{D-C}) (1 - \epsilon_{D-C})^2$$
 (11a)

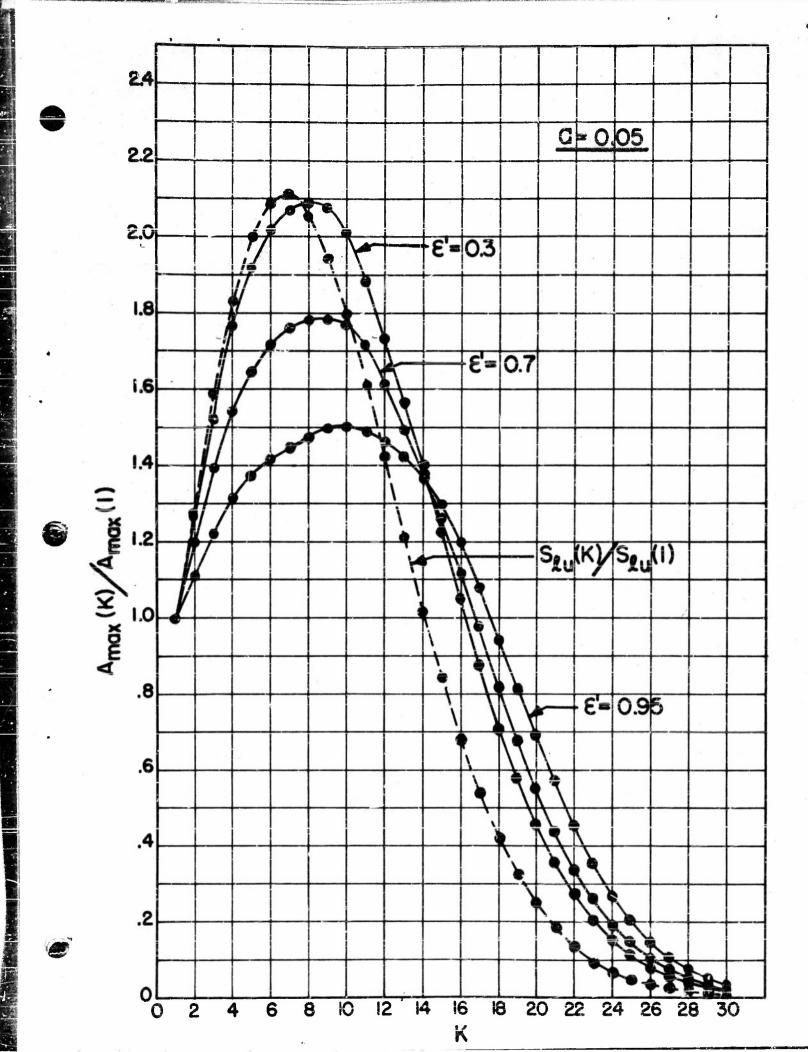
where \mathcal{E}_{D-C} and $\mathcal{E}_{D-C}^{\dagger}$ have been defined in Eqs. (13) and (13a). Comparison of Eqs. (9a) and (11a) shows that $I/RT_{\mathcal{E}} = I/I^{\dagger} - 1$ is obtained simply by reinterpreting the ordinates of Figs. 10 and 11. Hence the same conclusions apply to absorption experiments with discrete sources as to measurements of peak intensities for two-path experiments.

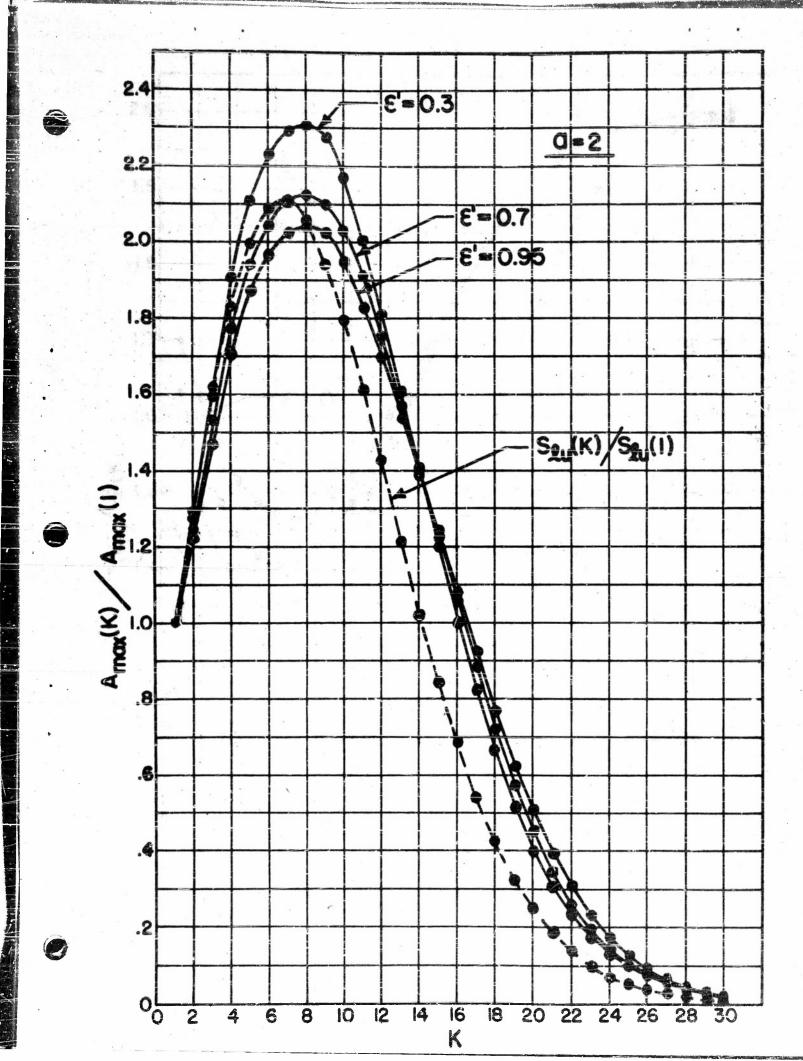
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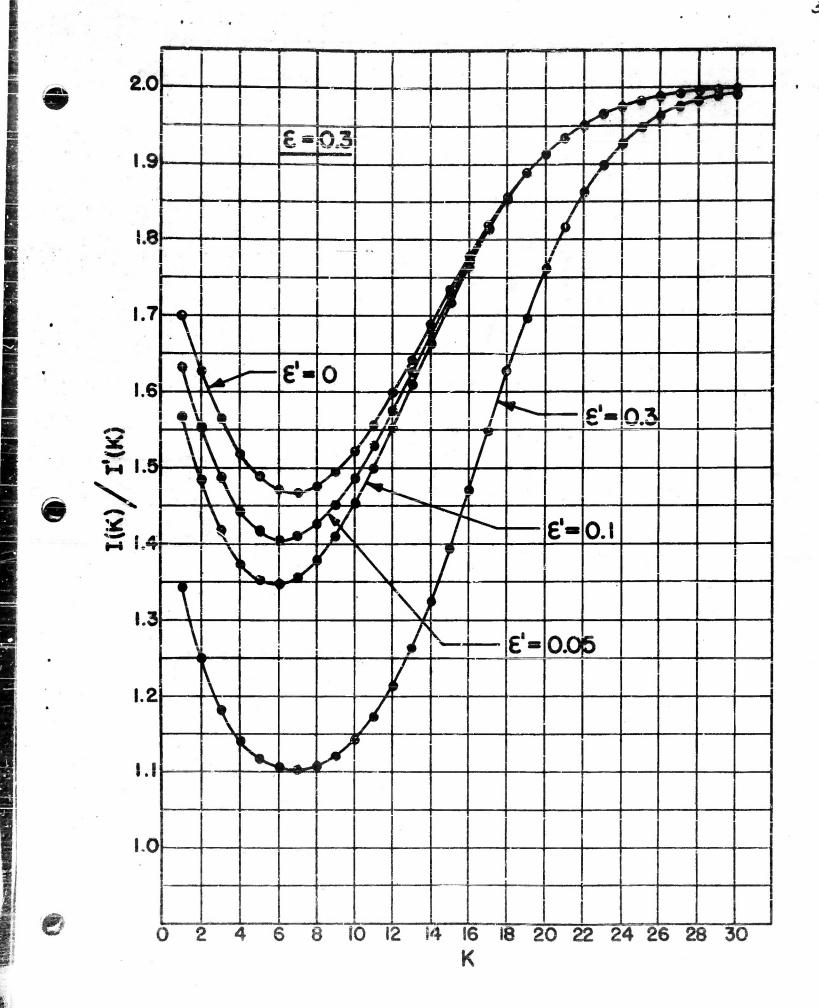
- Figure 1. The quantity A(a, K)/A(a, K) as a function of K for $K^{i} = 1$, a = 0.005.
- Figure 2. The quantity A(a, K)/A(a, K') as a function of K for K' = 1a = 0.05.
- Figure 3. The quantity A(a, K)/A(a, K') as a function of K for K' = 1, a = 2.
- Figure 4. Schematic arrangement of two-path experiment for a flame represented by two isothermal regions.
- Figure 5. The quantity I/I^t as a function of K for $\xi = 0.3$, $\xi^t = 0$, 0.05, 0.10, and 0.3.
- Figure 6. The quantity 1/1' as a function of K for $\xi = 0.5$, $\xi' = 0$, 0.16, 0.3, and 0.5.
- Figure 7. The quantity I/I' as a function of K for $\xi = 0.7$, $\xi' = 0$, 0.1, 0.3, 0.5, and 0.7.
- Figure 8. The quantity I/I' as a function of K for $\xi = 0.9$, $\xi' = 0$, 0.1, 0.3, 0.5, 0.7, and 0.9.
- Figure 9. Schematic arrangement of absorption experiment for a flame represented by two isothermal regions.
- Figure 10. The quantity I(K)/I'(K) as a function of K for $\xi = 0.7$, $\xi' = 0.1$, a = 0, 0.05, 0.3, 0.6, 2, and 10.

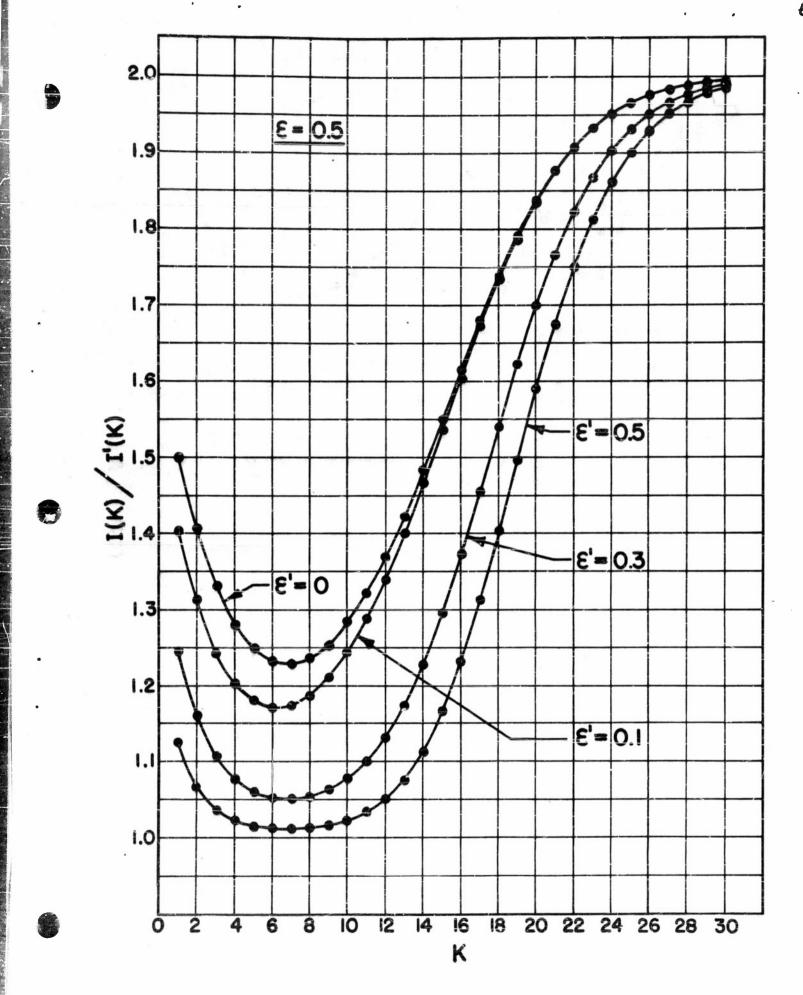
Figure 11. The quantity I(K)/I'(K) as a function of K for $\xi = 0.7$, $\xi' = 0.1$, a = 0, 0.05, 0.3, 0.6, 2, and 10.

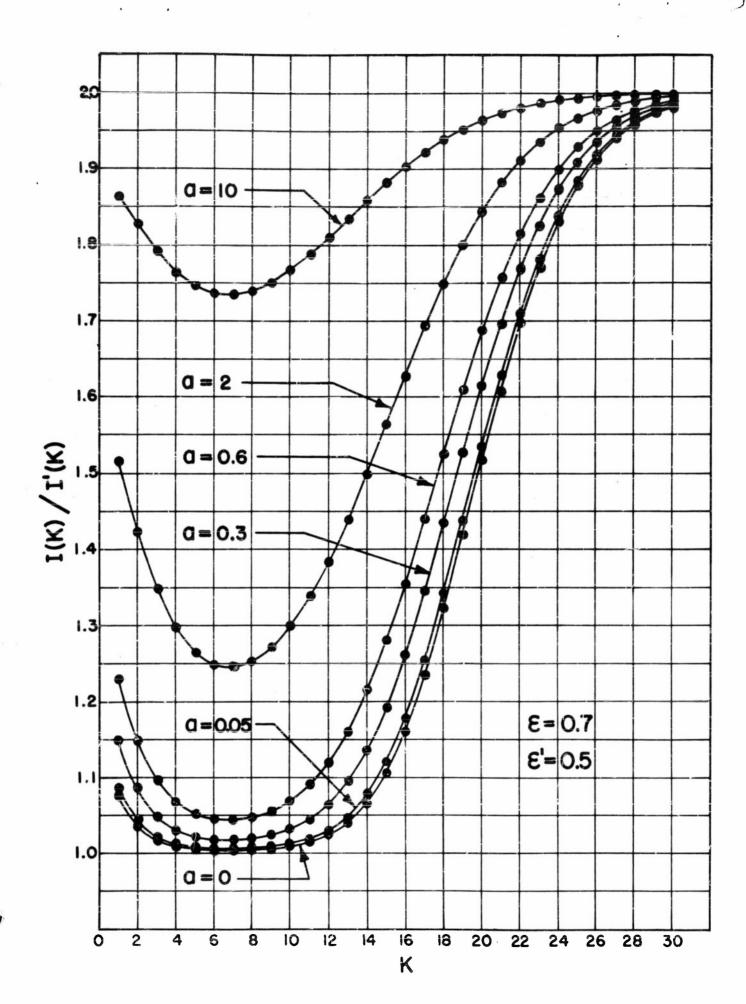


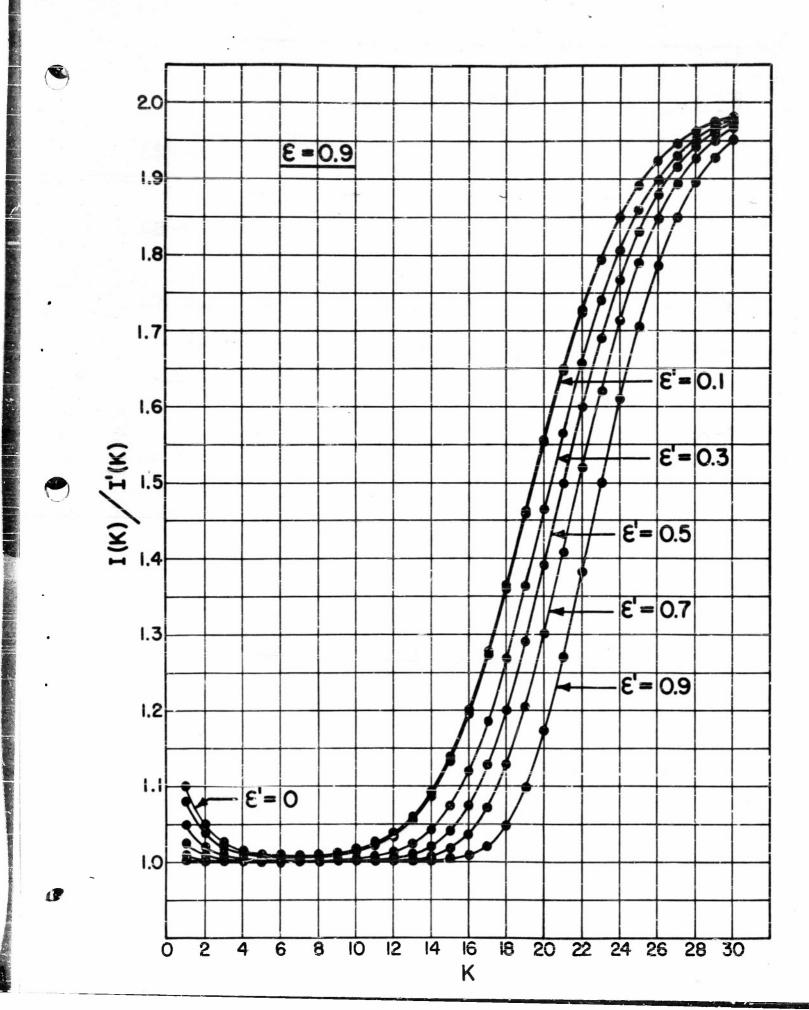


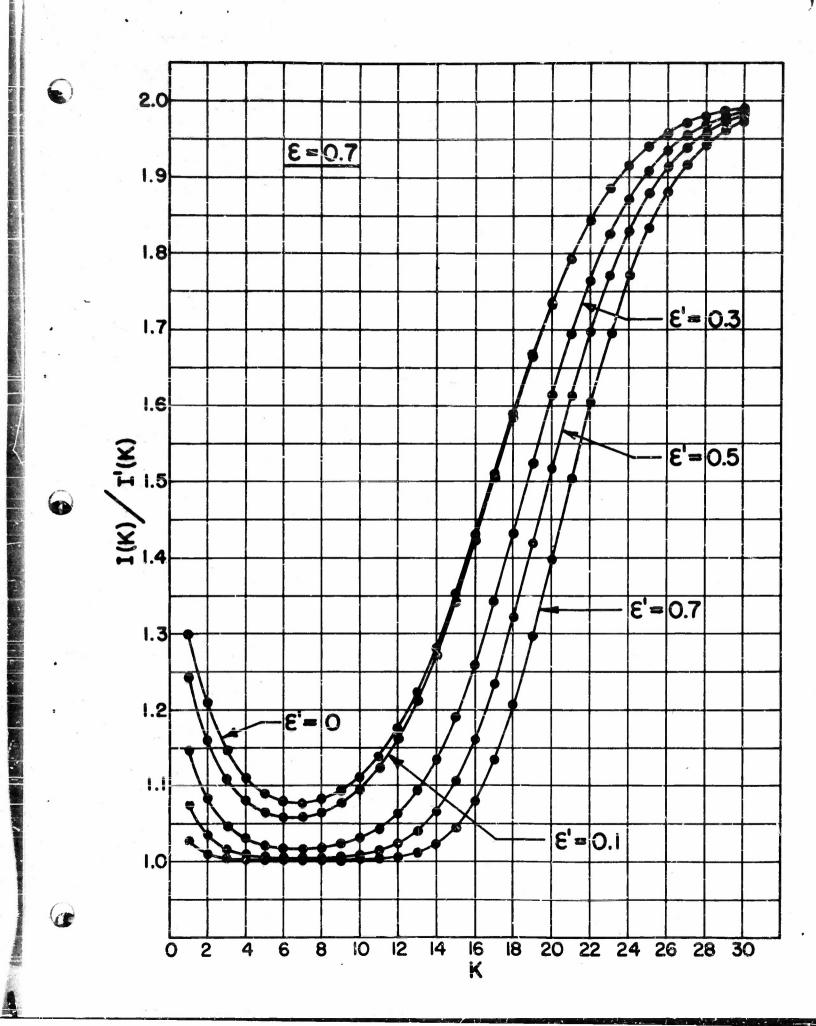




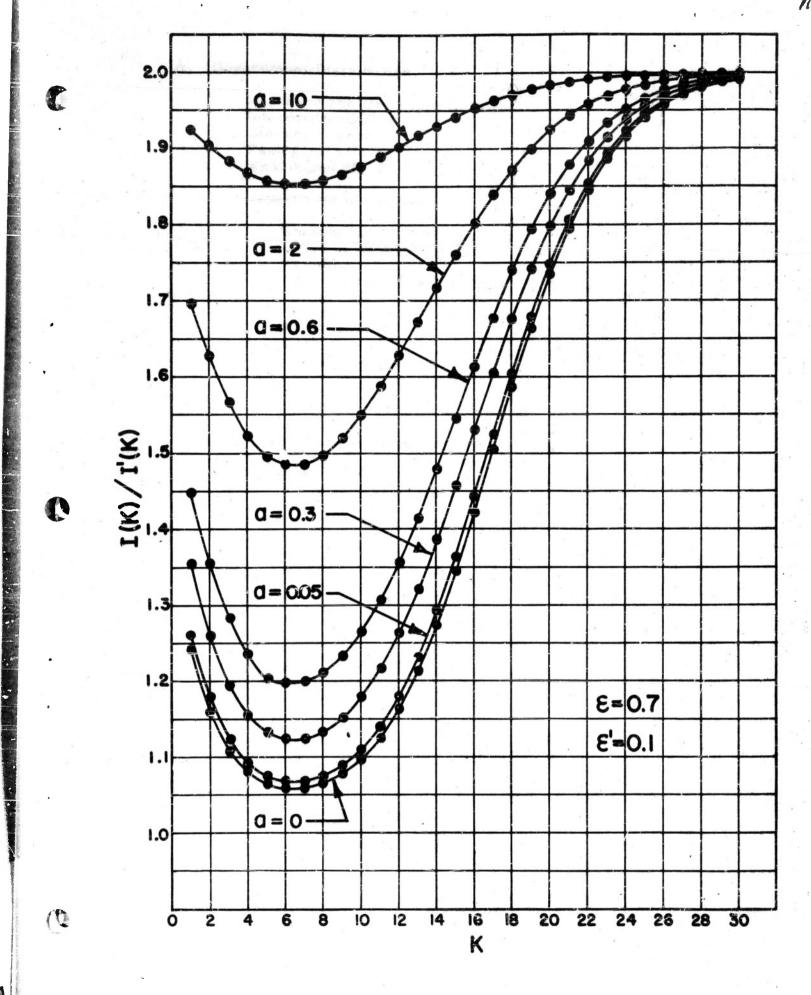












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